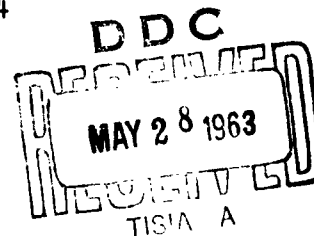63 3-5

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RESEARCH ON CdTe

M. R. Lorenz, R. E. Halsted and B. Segall
General Electric Research Laboratory
Schenectady, New York

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<u>RESEARCH ON CdTe</u>

M. R. Lorenz, R. E. Halsted and B. Segall
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I. GENERAL INTRODUCTION

In the last quarterly report we reported on the observation
of a double acceptor defect in CdTe by electrical transport
measurements on heat treated single crystals. During the present
reporting period we have studied the important emission process
in this material, which is the analogue of the "green edge
emission" in CdS. We have concluded that this emission process
involves the A_2 center. A model for the emission process has been
set up which provides an explanation for the properties of this
emission. Details of this study are given in Section II of this
report and have been published in Physical Review Letters, May 1,
1963.

We also reported on the e.p.r. spectrum of Cr substituted in
a Cd site in our last quarterly report. In Section III we give
the final version of this work as submitted and accepted for
publication in the Physical Review.

During the past reporting period we initiated an investigation
with regard to the production of the double acceptor (A_2) center
by electron bombardment. Several experiments to date have demon-
strated that bombardment of CdTe crystals with 1.5 Mev electrons
produces the A_2 center very much like the heat treatment does. We
are presently continuing this study in the hope of learning about
the nature and properties of more of these defects. It is most
interesting to note that the treatment of CdTe crystals by these
two different methods produce essentially identical results. This

confirms our previous assertion that the A_2 center is indeed an
intrinsic lattice defect. Further experiments are planned to
bring about a complete identification of the native center.

We have initiated some photoconductivity experiments on
n-type samples containing the A_2 center. Specifically we were
interested in whether band gap excitation is necessary to bring
about the trapping of holes on the A_2 center at low temperatures.
With the use of a series of band pass filters we have shown
excitation of the center to be effected by photons in the energy
range from approximately 1.0 to 0.3 ev. While radiation of band
gap or larger energy produces an almost instantaneous change,
longer wavelength radiation changes the $A_2^=$ center to A_2^- at a much
slower rate. Similarly the quenching of conductivity after the A_2
centers have been changed to the singly charged state A_2^-, i.e.,
$e^- + h\nu + A_2^- \rightarrow A_2^=$ proceeds at a very slow rate depending on the
energy of the photons as well as the total incident radiant power.
We can conclude from the present results that we can excite the
center, i.e., $A_2^= \rightarrow A_2^- + e^-$ (conduction band) with photons in the
range of about 1.0 to 0.3 ev, but much less efficiently than with
$h\nu \geq E$(band gap). The conductivity can be quenched in part by
low energy photons but very ineffectively. We wish to acknowledge
Dr. D. T. F. Marple for his cooperation in the photoconductivity
experiments.

II. DOUBLE ACCEPTOR FLUORESCENCE IN II-VI COMPOUNDS

by R. E. Halsted and B. Segall

DOUBLE ACCEPTOR FLUORESCENCE IN II-VI COMPOUNDS*

R. E. Halsted and B. Segall

We wish to show that the unique characteristics of a radiative recombination process, which has been observed to be prominent in the low-temperature emission of five II-VI semiconducting compounds, can be explained in terms of the properties of a native double acceptor defect recently identified in electrical transport measurements. We believe that this type of defect, with its characteristic fluorescent emission, will be found to occur more generally in compound semiconductors.

The most familiar example of this process is the "green edge emission" of CdS.[1-5] Analogs have been recognized in CdTe,[6] ZnSe,[7] ZnS,[8] and ZnO.[9, 2] In simplest form these fluorescent emission spectra are characterized by a temperature-dependent doublet structure, as illustrated in Fig. 1 for CdTe. This results from two closely spaced sets of emission lines, each set formed by the simultaneous emission of photons and 0, 1, 2, --longitudinal optical phonons. The high energy set becomes dominant with increasing temperature. Additional structure and polarization effects appear in wurtzite (hexagonal) crystals due to valence band splitting.

We wish to explain this emission process in terms of a native double acceptor, A_2, which has a doubly ionized level, $A_2^=$, close to the conduction band. The existence of $A_2^=$ levels 0.056 and 0.09 ev below the conduction bands of CdTe and CdS, respectively, has recently been established by the electrical transport measurements of Lorenz and Woodbury;[10] and more recently at a depth of ~ 0.1 ev in ZnSe by Aven.[11] That the observed $A_2^=$ levels in these materials are close to the conduction band is interesting in itself. Qualitatively this is understandable in terms of the tendency to reduce the mutual interaction of the extra electrons by a significant spreading of the wave function. This reduces $<r_{12}^{-1}>$ and allows for dielectric shielding. The competing attraction which acts to lower the level is of a covalent character which should decrease with the sequence CdTe to ZnS.

We attribute the lower energy set of the fluorescent emission peaks in Fig. 1 to recombination of an exciton bound to an A_2^- (alternatively, a hole bound to $A_2^=$). Unlike an electron whose capture at the A_2^- at low T is inhibited by a barrier, [10] an exciton can readily be captured or even created at the A_2. The higher energy set is associated with recombination of a hole which has become thermally dissociated from such a center.[1] Because of the considerable spread of the two electronic charges, the hole binding ($\approx$ doublet splitting, ΔE) is weak, reasonably comparable to exciton dissociation energies.

This correlation is based on two types of evidence: The emission energy is relatively constant (compared to the band gap) with changing temperature, in
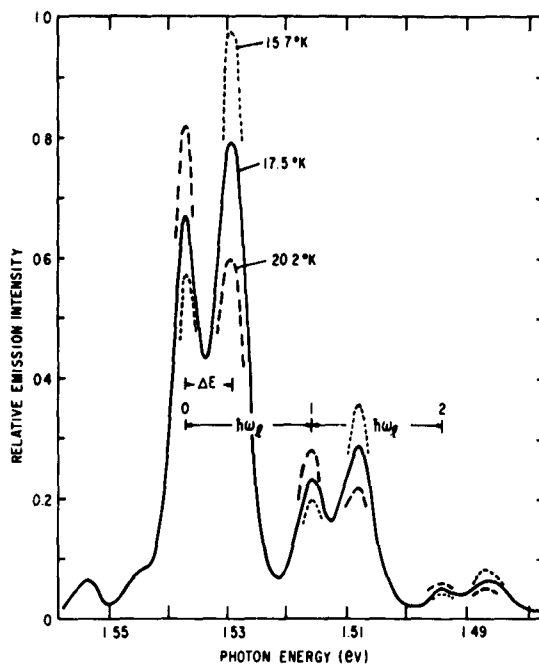

Fig. 1 Temperature-dependent doublet structure in fluorescent emission spectrum of CdTe attributed to transitions involving a native acceptor with a doubly ionized level near the conduction band.

TABLE I

Summary of Relevant Data from Fluorescent Emission and Transport Measurements in II-VI Compounds

	CdTe	CdS	ZnSe	ZnS	ZnO
E_g (4°K)	1.606 ev[a]	2.582 ev[d]	2.838 ev[g]	3.84 ev[j]	3.44 ev[l]
E_g (T)	1.593 (100°K)[b]	2.50 (250°K)[b,e]			
E_g (T) - $E_{Th}(A_2^=)$	0.056 (100°K)[c]	0.09 (250°K)[c]	~0.1 (0°K)[h]		
$E_{Th}(A_2^=)$	1.54	2.41	~2.7		
$E_{op}(A_2^=)$	1.54[a]	2.41[f]	2.70[i]	3.64[j]	3.35[m]
$\Delta E_{op}(A_2^=)/\Delta E_g$	<0.2 (0°-80°K)[b]	<0.3 (0°-100°K)[b,e]	<0.4 (0°-80°K)[i]	1[k]	
ΔE [doublet splitting]	0.009[b]	0.019[f,b]	0.015[i]	0.044[j]	0.04[m]
T [doublet peaks = intensity]	20°K[b]	30°K[f,b]	20°K[i]	75°K[j]	
T [intensity 1% of 20°K value]	80°K[b]	115°K[f,b,e]	100°K[b]	120°K[j]	

a. Ref. 6
b. Present work
c. Ref. 10
d. Ref. 3
e. Ref. 5
f. Ref. 4
g. Ref. 13
h. Ref. 11
i. Ref. 7
j. Ref. 8
k. Footnote †, p. 3
l. Ref. 14
m. Ref. 9

agreement with the picture of transitions between an acceptor level and the valence band. The positions of the levels derived from emission and transport data agree in the three compounds in which such a comparison is possible: CdTe, CdS, and ZnSe.

Values of $\Delta E_{op}(A_{\bar{2}})/\Delta E_g$ appreciably less than unity in Table I illustrate the fact that the change of position of the emission peak, $\Delta E_{op}(A_{\bar{2}})$, is less than the change in band gap, ΔE_g, over the specified temperature range. This is clearly evident in samples with structure sufficiently well resolved to prevent misinterpreting a change of relative intensity of adjacent emission peaks as a shift in position.*† That the $A_{\bar{2}}$ level is relatively fixed with respect to the valence band is best understood in terms of its identification as an acceptor; e.g., the triply ionized Cu acceptor in Ge exhibits such behavior.[12]** Consequently, the electron binding energy $[E_g(T) - E(A_{\bar{2}})]$ is quite T-dependent, and depths derived from transport data are appropriate only for a specific T.‡

Data permitting a comparison of optical and thermal determinations of $E(A_{\bar{2}})$ are given in Table I. The difference between the depth $[E_g(T) - E_{Th}(A_{\bar{2}})]$ and $E_g(T)$ at the indicated T yield the thermal position, $E_{Th}(A_{\bar{2}})$, relative to the valence band. $E_g(4°K)$ is known within ~0.001 ev from the exciton position and binding energy. $E_g(T)$ was determined by measurements of the T-dependence of near band edge radiation which will be reported elsewhere. The two measurements of level position agree within experimental precision for CdTe, CdS, and ZnSe.

Other unique aspects of the emission can also readily be understood in terms of the proposed mechanism. The T-dependence of the intensity ratio, R(T), of the higher to lower energy doublet peaks is consistent with transitions involving continuum and bound states, respectively. The ratio can be shown to be approximately

$$R(T) = |F(0)|^{-2}(n_f/n_b)N_{A_2} \approx \pi a^3 N_{A_2} N_V N^{-1} e^{-\Delta E/kT} \tag{1}$$

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*Our prior data on this emission in CdTe[6] was in error on this point for this reason. A similar problem was resolved in CdS.[4]

†The line breadth and scatter of published emission data on ZnS would allow a ratio significantly below the value of unity cited.[8]

**$E(A_{\bar{2}})$ would be more T-dependent when $E_g(T) - E(A_{\bar{2}})$ becomes relatively small, i.e., at high T and for large gaps.

‡In a region in which the depth is linear in T, an analysis of the slope of n vs 1/T gives the extrapolated 0°K depth. On the other hand, analysis of a step of magnitude $\Delta n(= n_2 - n_1)$ in an n vs 1/T plot gives the depth appropriate to the T at which $n = n_1 + \Delta n\, g(1 + g)^{-1}$ where g is the degeneracy factor of the level. See Fig. 3, Ref. 12, where a value g = 1 was used.

where n_f/n_b is the ratio of free to bound holes, N_{A_2} is the concentration of A_2 centers, $F(0)$ and $\underline{a}$ the envelope function and characteristic radius for the bound hole, N_v the valence band density of states, and N a quantity which depends among other things on the effectiveness of the competing processes. With the plausible value of $N \approx 10^{13} \mathrm{cm}^{-3}$ for the CdTe measurements and a "hydrogenic" value of 80 A for $\underline{a}$, reasonable agreement with the data in Fig. 1 is achieved. The large N_v enhances the probability of the higher state at low T (i.e., $T \ll \Delta E/k$). If both states were either bound or free, $R(T) \approx e^{-\Delta E/kT}$ and could be unity only at much higher T than cited in Table I.

In Table I, temperatures are given representative of the region in which the emission intensity drops rapidly to zero. On the other hand, emission lines closer to E_g, which can be attributed to exciton recombination, persist to substantially higher temperatures. The energy required to convert ($A_2^=$ + hole) into (A_2^- + exciton) is less than the $E_g(T) - E(A_2^=)$ by the free exciton binding energy. The lower T of disappearance of the emission of interest is therefore understandable and should be ordered in different compounds with the $E_g(T) - E(A_2^=)$ as is observed.

The emission intensity correlates qualitatively with conditions favoring the presence of A_2 centers. Its occurrence in multiply zone-refined CdTe and in CdS of highest purity suggests that a native defect is involved. In CdTe crystals doped with donor impurities the emission energy is lowered, while in acceptor doped crystals it is raised.[6] These shifts occur in directions consistent with the perturbation of the $A_2^=$ level downward by nearby ionized donors and upward by ionized acceptors.

The systematics and occurrence of the basic doublet emission structure in both wurtzite and zinc blende crystals rule out its explanation in terms of valence band splitting. The predicted structure with this origin in wurtzite crystals[2] should be evident as an additional emission set appearing at sufficiently high T. Data on ZnO exhibit the three emission sets.[9] The no-phonon lines at 3.31 and 3.35 ev observed with $\epsilon \perp$c-axis are the transitions involving the bound hole and free hole in the $\Gamma_5(x, y)$ valence band. Their nearly equal intensities at $T = 90°K$ is understandable in terms of Eq. (1). The 3.38 ev transition observed with $\epsilon \parallel$c involves the free hole in the $\Gamma_1(z)$ valence band, and its relative intensity is given by $\exp(-E_{51}/kT)$ as observed, where E_{51} is the valence band splitting.

Thus it can be seen that the specific concept of a doubly ionized native acceptor level near the conduction band, coordinating transport and fluorescence measurements, provides a basis for a detailed understanding of the characteristics of this class of spectra in II-VI compounds. The correlation of this acceptor with a specific native defect, speculative on the basis of the present data, merits further attention. Since the above compounds are broadly representative of the II-VI family, one would expect similar transport and fluorescent properties in the other compounds in the family. In fact, analogous behavior would also be anticipated in other semiconductors, e.g., the III-V compounds.

ACKNOWLEDGMENTS

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III. PARAMAGNETIC RESONANCE OF CHROMIUM IN CdTe

by G. W. Ludwig and M. R. Lorenz

Paramagnetic Resonance of Chromium in CdTe*

G. W. Ludwig and M. R. Lorenz

I. INTRODUCTION

The technique of electron paramagnetic resonance has been used with moderate success for the study of defect centers, principally transition metal ions of the 3d group, in CdTe and related II-VI compounds. Data on manganese ions having a half-filled 3d shell is available for all of these compounds, while cobalt in the $3d^7$ configuration has been studied in most of them. Paramagnetic resonance associated with chromium has been reported only in ZnS and CdS.[1,2]

The purpose of the present paper is to report on the paramagnetic properties of chromium in the $3d^5$ configuration in CdTe, a cubic crystal having the zincblende structure. If chromium were simply to substitute for cadmium in the lattice with no charge unbalance, its configuration would be expected to be $3d^4$. The fact that one detects $Cr(3d^5)$ implies that chromium can act as an acceptor as it does in ZnS.[1,3] The resonance study of $Cr(3d^5)$ in CdTe has been unusually successful. It has been possible to determine not only the g factor and the cubic field splitting parameter, but also, using electron-nuclear double resonance (ENDOR) techniques, the hyperfine interaction with Cr^{53}, and the complete tensor describing the hyperfine coupling with the magnetic isotopes Cd^{111} and Cd^{113} occupying second neighbor

positions.

Sample preparation and properties and the resonance spectrum are described in II; III is devoted to a description of the ENDOR experiments; the results are presented and discussed in IV.

II. EXPERIMENTAL TECHNIQUES AND THE RESONANCE SPECTRUM

High purity CdTe single crystals were prepared by techniques already described.[4] Samples were cut into oriented bars approximately $3 \times 3 \times 10$ mm^3 with a [110] axis parallel to the long dimension. The bars were etched in $HF \cdot HNO_3 \cdot 2H_2O$ solution and chemically polished in a solution of 70 parts of saturated $K_2Cr_2O_7$ and 30 parts of concentrated H_2SO_4.[5] The latter solution apparently gives rise to an adsorbed layer of chromium ions which is not completely removed even by a thorough rinse in distilled water. The treated bars were sealed in evacuated quartz ampoules to which Cd metal had been added. These were held for 24 hours or longer at 950°C, were quenched, and the surface regions were removed. The Hall coefficient resistivity and Hall mobility were measured from 12 to 350°K using conventional techniques.

A number of samples were n-type and exhibited electron freezeout into a level 0.056 eV below the conduction band[6] and also into the hydrogenic donor level.[7] When such samples were examined in a paramagnetic resonance spectrometer which

has been described previously,[8,9] resonant absorption was detected in the vicinity of g = 2. The spectrum was not observed if the Fermi level locked onto a level 0.6 eV below the conduction band edge. Thus, the resonant center must have an electrical level located within 0.6 eV of this band edge.

With the magnetic field H restrained to be in the (110) plane, the resonance spectrum, shown in Fig. 1, is simplest for H in a zero cubic field splitting direction. (This is the direction in which p vanishes, where

$$p = 1 - 5(l^2 m^2 + m^2 n^2 + n^2 l^2) \tag{1}$$

l, m, and n being the direction cosines of the magnetic field with respect to the cubic crystalline axis). For p = 0 the spectrum consists of seven strong resolved lines having an envelope of intensities. A similar pattern has been described previously for resonant centers in CdS[10] and CdTe[11], and has been attributed to an essentially isotropic hyperfine coupling of the unpaired electrons with the magnetic isotopes Cd^{111} and Cd^{113} occupying twelve equivalent sites, viz. the twelve nearest Cd sites to an impurity ion occupying a substitutional Cd site.

As the magnetic field is rotated in the (110) plane towards p = 1 (the [001] direction), each of the Cd hyperfine lines splits into three resolved fine structure components. However, if there were only three fine structure components (S = 3/2) one would expect no cubic field splitting. One

is thus led to suspect that S = 5/2: there are five fine
structure components but the splitting between the outer
fine structure components is not resolved. Taking for
the spin-Hamiltonian

$$\mathcal{H} = g\beta S \cdot H + (1/6)a \; [S_x^4 + S_y^4 + S_z^4 - (1/5)S(S+1)(3S^2+3S-1)] \quad (2)$$

and assuming S = 5/2 and $|a| \ll g\beta S \cdot H$, the $\Delta M = \pm 1$ transitions
are given by:

$$M = +1/2 \text{ to } -1/2: \quad h\nu = g\beta H$$
$$M = \pm 3/2 \text{ to } \pm 1/2: \quad h\nu = g\beta H \mp (5/2)pa \quad (3)$$
$$M = \pm 5/2 \text{ to } \pm 3/2: \quad h\nu = g\beta H \pm 2pa$$

where p is defined by (1).

From the spectrum for p = 0 one finds g = 1.9997 $\pm$0.0003.
Similarly from analysis of the angular dependence of the
fine structure components we obtain $|a| = (3.1 \pm 0.6) \times 10^{-4}$cm.
In arriving at this value it was assumed that the experi-
mentally measured peak position of the outer fine structure
components represented the $\pm 3/2$ to $\pm 1/2$ transitions, which
are stronger than the $\pm 5/2$ to $\pm 3/2$ transitions and which
generally also are narrower. The large uncertainty takes
into account the possible inaccuracy of this assumption.

Impurity ions in CdTe which might have electron spin 5/2
are Cr, Mn, and Fe. To check whether the above spectrum is
associated with Cr($3d^5$) a sample was prepared containing
chromium enriched in the isotope Cr^{53}, which has a nuclear

spin of 3/2. Indeed a spectrum was detected in this sample
which was similar to that of Fig. 1 except that there were
13 strong lines for p = 0 instead of 7. Thirteen strong
lines are to be expected if the hyperfine interaction with
the Cr^{53} nucleus is roughly twice as large as that with the
neighboring Cd^{111} and Cd^{113} nuclei.

III. ENDOR MEASUREMENTS

In order to gain additional information about the hyper-
fine interaction with Cr^{53} and with the magnetic Cd isotopes
the sample was examined using the electron-nuclear double
resonance (ENDOR) technique developed by Feher.[12] In this
technique, one detects transitions in which a nuclear spin
reorients, the electron spin retaining its orientation
($\Delta M = 0$, $\Delta m = \pm 1$), via the associated change in intensity
of an electron paramagnetic resonance line. Experimentally,
one adjusts the magnetic field to resonance on an electron
paramagnetic resonance line and simultaneously exposes the
sample to an rf magnetic field which induces the nuclear
transitions. In analyzing the ENDOR transitions, we assume
that the nuclear sub-levels are described by the Hamiltonian.

$$\mathcal{H}_N = A \, S \cdot I - \gamma \beta_N H \cdot I + \sum_k (S \cdot T_k \cdot I_k - \gamma_k \beta_N H \cdot I_k). \tag{4}$$

Here the first two terms describe the isotropic hyperfine
interaction with Cr^{53}, while the kth of the remaining terms
give the anisotropic interaction with Cd^{111} or Cd^{113}
occupying the kth of the nearest Cd neighbor positions to the

impurity site.

A. Cr[53]

Supplementing (2) with (4) and assuming the hyperfine interaction terms to be small, one finds that the frequency f of a Cr[53] ENDOR transition is approximately

$$hf = |AM -[S(S+1)+(2m-1)M-M^2] \; (A^2/h\nu) \; -\gamma\beta_N H \;| \tag{5}$$

Since S = 5/2, M can take on the values $\pm 1/2$, $\pm 3/2$, $\pm 5/2$, while for I = 3/2 there are three m to m-1 transitions. Thus one has the possibility of detecting eighteen ENDOR transitions of widely differing frequencies from which the two parameters A and γ are to be determined. Of these eighteen transition, we have studied all but the M = +5/2 transitions, which are weak because of the Boltzmann factor. The M = -5/2 transitions are shown in Fig. 2. The value for A (including its sign, which can be determined knowing the signs of M and γ) and a value for γ, the nuclear g factor of Cr[53] are given in IV. In addition, the experimentally determined magnitude of the second order terms in (5) confirms the supposition that S = 5/2.

B. Cd[111] and Cd[113]

The analysis of the Cd[111] and Cd[113] ENDOR spectrum is more involved than the Cr[53] analysis because the Cd hyperfine interaction tensor is anisotropic. Since Cd[111] and Cd[113] each have nuclear spin 1/2, one has only the m = 1/2 to -1/2 transition. However, besides the six values of M there

are twelve values of k. For the magnetic field in the (110)
plane, one can show by symmetry that the twelve k yield
seven spectra of relative intensity 1:1:2:2:2:2:2. Moreover
in high symmetry directions some of these seven coalesce; for
example, in the [110] direction one has four spectra of
intensity 2:2:4:4.

The detection of the Cd ENDOR transitions is a relatively
difficult experimental problem because of the low natural
abundance of the relevant isotopes (Cd^{111} and Cd^{113} are
12.7°/o and 12.3°/o abundant, respectively). ENDOR transi-
tions have been detected for all k only for M = -3/2 and
H in the [$\bar{1}$10] direction. For Cd^{113} these transitions are
at 20.42, 20.51, 21.04, and 21.12 Mc/sec. The analysis of
this spectrum will now be described.

The second neighbors to a substitutional site in the
CdTe lattice lie in the (110) planes, which are planes
of reflection symmetry. As a result one of the principal
axes of the tensor describing the hyperfine interaction of
the Cr(3d^5) center with its nearest Cd neighbors (which occupy
the 220 positions) is the corresponding [110] direction.
The other two principal axes lie in the corresponding (110)
plane (see Fig. 3). Since the magnetic interaction between
the Cd nucleus and the unpaired electrons is strong compared
to the nuclear Zeeman interaction (gβS·H>>S·T$_k$·I$_k$>>$\gamma_k\beta_N$H·I$_k$),
the Cd^{113} ENDOR transitions are given approximately by

$$hf = | MT_k - \gamma_k \ \beta_N H(T_1 \cos^2 \theta_1 + T_2 \cos^2 \theta_2 + T_3 \cos^2 \theta_3)/T_k | \qquad (6)$$

where γ_k is the nuclear g factor of Cd^{113} and θ_i is the angle between the magnetic field and the ith principal axis of the tensor T_k. For H in a $[\bar{1}10]$ direction, the four possible T_k, having intensities 2:2:4:4, are as follows:

$$T_a = T_3 \tag{7}$$

$$T_b^2 = T_1^2 \cos^2\beta + T_2^2 \sin^2\beta \tag{8}$$

$$4T_c^2 = 2T_1^2 [(\cos\beta/\sqrt{2}) - \sin\beta]^2 + 2T_2^2 [(\sin\beta/\sqrt{2}) + \cos\beta]^2 + T_3^2 \tag{9}$$

$$4T_d^2 = 2T_1^2 [(\cos\beta/\sqrt{2}) + \sin\beta]^2 + 2T_2^2 [(\sin\beta/\sqrt{2}) - \cos\beta]^2 + T_3^2 \tag{10}$$

Equations (7)-(10) are four equations in the four unknowns T_1, T_2, T_3, and β. There is the additional uncertainty that experimentally one does not know which of the two weaker ENDOR transitions is described by (7) and which by (8). (With the convention $T_1 > T_2$, this single choice serves to allocate the measured transitions among (7)-(10)). If one assigns the transitions at 20.42, 21.04, 20.51, and 21.12 Mc/sec to T_a, T_b, T_c, and T_d, respectively, and substitutes into (6), one obtains the hyperfine parameters quoted in IV.[13] By interchange of T_a and T_b one obtains $T_1 = +5.77$, $T_2 = +5.55$, $T_3 = +5.75$, all in units of $10^{-4}cm^{-1}$, and $\beta = 60°$. This result is considered unlikely because of the large angle between the axis of T_1 and the Cr-Cd internuclear axis, which corresponds to $\beta = 0$.

IV. RESULTS AND DISCUSSION

The parameters of the complete spin Hamiltonian (2) plus (4) at 1.4°K determined as described in II and III are:

$S = 5/2$

$g = 1.9997 \pm 0.0003$

$|a| = (3.1 \pm 0.6) \times 10^{-4} cm^{-1}$

$A = (+12.781 \pm 0.005) \times 10^{-4} cm^{-1}$ } for Cr^{53}

$\gamma = 0.3161 \pm 0.0008$

$T_1 = (+5.82 \pm 0.05) \times 10^{-4} cm^{-1}$

$T_2 = (+5.63 \pm 0.05) \times 10^{-4} cm^{-1}$ } for Cd^{113}

$T_3 = (+5.61 \pm 0.05) \times 10^{-4} cm^{-1}$

$\beta = 37 \pm 5°$

The magnitude of γ given above agrees within the experimental error with published values of γ for Cr^{53} but not with γ for any other common nuclide. Thus the center under study undoubtedly is a chromium ion. Since $S = 5/2$ and $g \simeq 2$ it seems clear that the chromium ion has a half-filled 3d shell. Moreover the magnitudes of g, a, and A are similar to those reported by Title for $Cr(3d^5)$ in cubic ZnS.[1]

The number and relative intensities of the hyperfine lines shown in Fig. 1 are consistent with the notion that the hyperfine interaction is with Cd^{111} and Cd^{113} occupying twelve equivalent sites. The ENDOR spectrum discussed in III B confirms this notion. If the chromium were substituted for Te in the lattice it would have four nearest Cd neighbors (the hyperfine interaction with these would be expected to be larger than that with the twelve Cd neighbors at the 311 positions).

If the chromium ion were interstitial, it would have either four or six nearest Cd neighbors. Agreement with the spectrum is obtained only if one assumes that the chromium substitutes for Cd, in which case it does have twelve nearest Cd neighbors.

Chromium which substitutes for Cd in the lattice and has the configuration $3d^5$ must have accepted an electron.[3] The electrical measurements referred to in II show that the acceptor level lies within 0.6 eV of the conduction band edge.

Superhyperfine interaction with Cd in the 220 positions has been observed previously for $Mn(3d^5)$ in CdS[10] and $CdTe$.[11] The hyperfine splitting which we observe ($\sim$6 gauss) for $Cr(3d^5)$ is roughly four times as large. Thus the wave function of the $Cr(3d^5)$ center is more spread out, which might be expected since the Cr center has trapped an electron. The principal axes of the Cd hyperfine interaction are as given in Fig. 3.

Unfortunately, the hyperfine interaction with tellurium neighbors to the Cr center was not detected. Thus, one cannot decide experimentally how the wave function of the Cr center is divided among the Te and Cd sublattices. No explanation is offered for the magnitude of the anisotropy of the Cd hyperfine coupling.

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2. For a more complete discussion of paramagnetic resonance of defects in II-VI compounds, including references, see G. W. Ludwig and H. H. Woodbury, Solid State Physics $\underline{13}$, 223 (1962).

3. The configuration of the free chromium atom is $3d^5 4s$. On an ionic model one writes CdTe as $Cd^{2+}Te^{2-}$; thus at a chromium impurity site, assuming no charge unbalance, one would have $Cr^{2+}(3d^4)$. On a covalent model one writes CdTe as $Cd^{2-}Te^{2+}$, but the outer Cd electrons are used in the covalent bonding. On such a model one would have $Cr^{2-}(3d^4 4s 4p^3)$ at a chromium site were there no charge unbalance. The $4s4p^3$ electrons participate in covalent bonding leaving the Cr core in the $3d^4$ configuration. Thus with either model $Cr(3d^4)$ is the configuration for no charge unbalance at the Cr site, while $Cr(3d^5)$ implies that the chromium impurity has accepted one electron.

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13. The frequency range in which the ENDOR transitions occur is such that agreement with the hyperfine splitting of Fig. 1 is obtained only if $M = 3/2$ and in addition the first and second terms of (6) tend to cancel. Since the $M = +3/2$ level is depopulated we assume that the transitions correspond to $M = -3/2$. The cancellation of the terms in (6) then implies that γ_k and the components of T_k have opposite signs, from which we conclude that the components of T_k are positive.
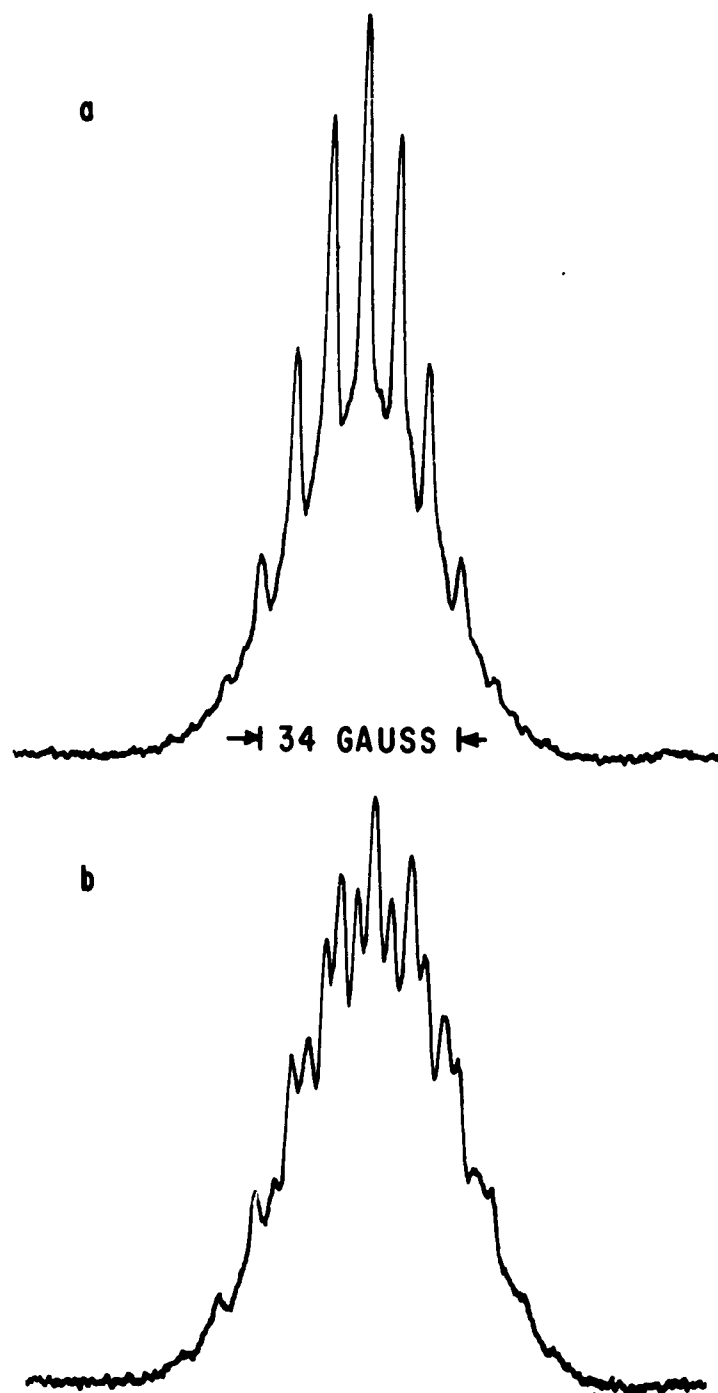
Fig. 1 Spectrum of Cr($3d^5$) in CdTe at 4.2°K with the spectrometer tuned to dispersion under rapid passage conditions. (a) H in the zero cubic field splitting direction (p = 0). (b) H in a [001] direction.
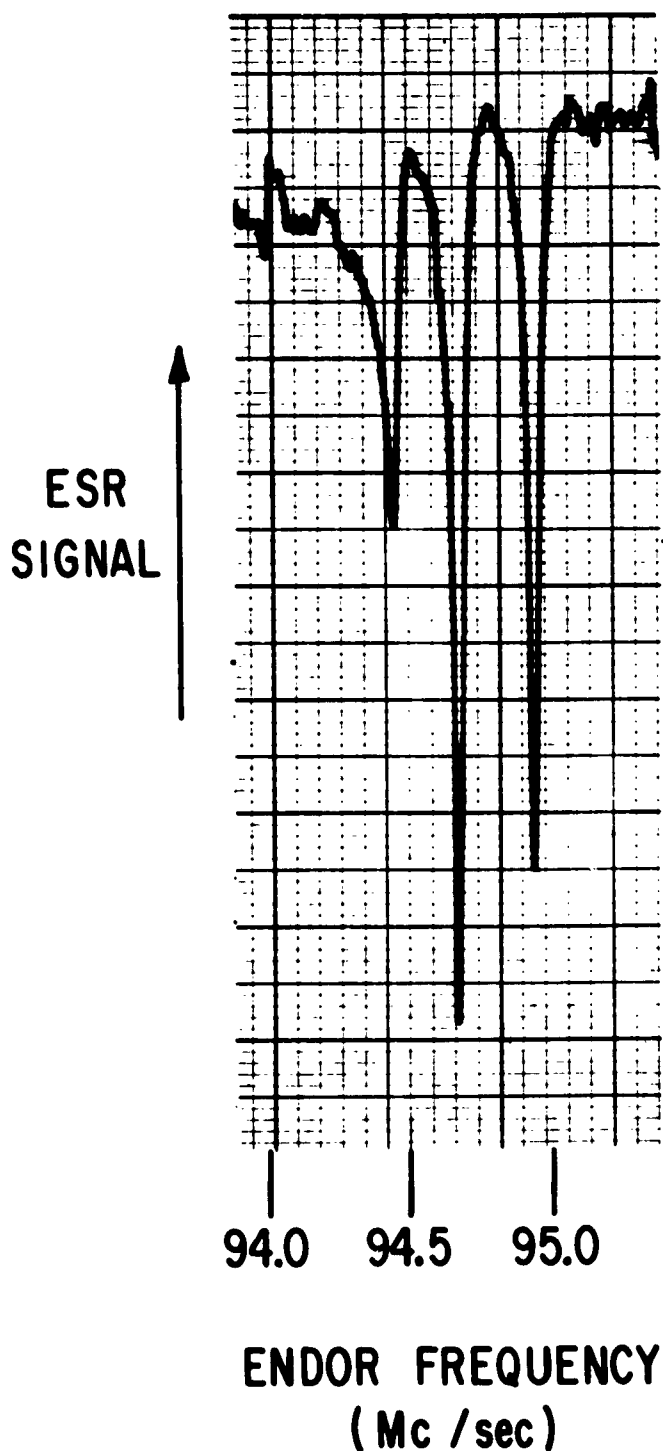
ESR
SIGNAL

94.0 94.5 95.0

ENDOR FREQUENCY
(Mc /sec)

Fig. 2 Endor transitions of the
Cr^{63} impurity nucleus for
$M = -5/2$. The three lines
correspond to the three possible
m to m-1 transitions for $I = 3/2$,
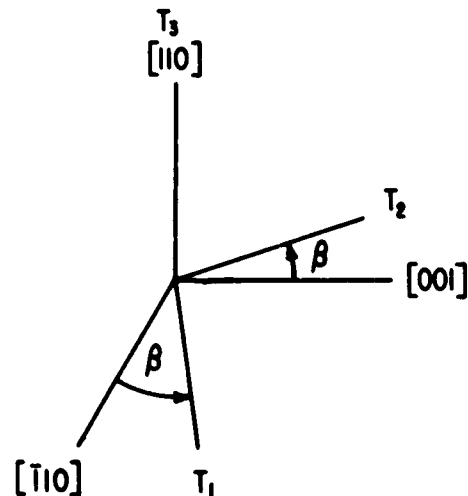as described by (5).

Fig. 3 Principal axes of the
tensor describing the hyperfine
coupling between the Cr center
and its nearest Cd neighbors.
Experimentally we find β =
$37 \pm 5°$, using the convention
$T_1 > T_2$.

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ARA (Mrs. Koch)
c/o D. C. Reynolds
Research Physicist
Solid State Physics Research Branch
Aeronautical Research Laboratory
Wright-Patterson AFB, Ohio

ARA (Library)
c/o D. C. Reynolds
Research Physicist
Solid State Physics Research Branch
Aeronautical Research Laboratory
Wright-Patterson AFB, Ohio

EWAPL (Library, Area B)
c/o D. C. Reynolds
Research Physicist
Solid State Physics Research Branch
Aeronautical Research Laboratory
Wright-Patterson AFB, Ohio

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